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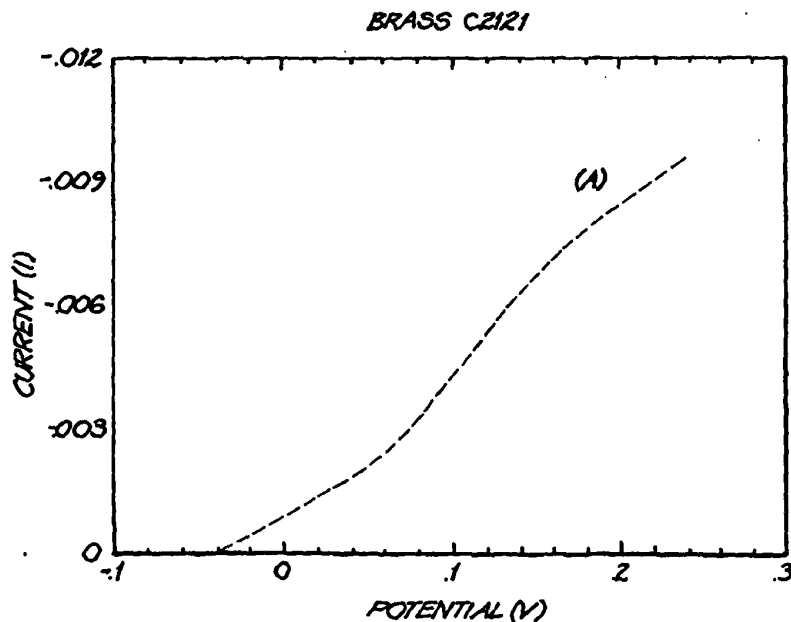
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(54) Title: A BIOCIDAL CORROSION INHIBITING COMPOSITION



(57) Abstract

A corrosion inhibiting composition for use in combination with a strong oxidising agent is disclosed. The corrosion inhibiting composition comprising at least one aromatic triazole, at least one molybdate salt and at least one nitrate salt. A method of cleaning and sterilising a surface by contacting the surface with a strong oxidising agent and a corrosion inhibiting composition is also disclosed.

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## A BIOCIDAL CORROSION INHIBITING COMPOSITION

**Technical Field**

This invention relates to a corrosion inhibiting composition, and in particular, to a corrosion inhibiting composition for use with a strong  
5 oxidising agent.

**Background Art**

The invention is particularly applicable for sterilising medical instruments which may include brass, copper, aluminium, stainless steel, carbon steel and plastic parts.

10 As will be clear to a person skilled in the art, strong oxidising solutions can cause corrosion in a variety of metals. This is of particular concern in the medical field where strong oxidising solutions are used to sterilise medical equipment. The equipment is, for example, immersed in a bath of oxidising solution, such as an aqueous solution of stabilised  
15 hydrogen peroxide, activated glutaraldehyde, chlorine dioxide or chlorine solution. The solution can cause surface or local corrosion of metal parts of the medical instruments.

Sterilisation is, of course, required however it is desirable to eliminate or at least reduce corrosion.

20 Throughout this specification, unless the context requires otherwise, the word "comprise", or variations such as "comprises" or "comprising" will be understood to imply the inclusion of a stated element or integer or group of elements or integers but not the exclusion of any other element or integer or group of elements or integers.

**25 Disclosure of the Invention**

In a first aspect the present invention provides a corrosion inhibiting composition for use in combination with a strong oxidising agent, said composition comprising at least one aromatic triazole, at least one  
30 molybdate salt and at least one nitrate salt. The preferred aromatic triazoles are benzotriazole and tolyltriazole, benzotriazole being more preferred. The preferred molybdate salts are alkali metal salts such as sodium molybdate. The preferred nitrate salts are alkali metal salts such as sodium nitrate.

The corrosion inhibiting composition may include a free-flow agent such as silicon dioxide. Silicon dioxide is suitable as it is inert in oxidising  
35 solutions. Fumed silicon dioxide improves flow properties of the composition when the composition is in powder form and also gives

improved dispersion and solubilisation of the powder in water. It is theorised that this is due to an alteration in electrostatic charge and prevention of attractive forces thus inhibiting clumping. The particle surface change from hydrophobic to hydrophilic allows rapid penetration of water through the powder thereby improving solubility.

In a second aspect the present invention provides a biocidal composition comprising a strong oxidising agent and a corrosion inhibiting composition, said corrosion inhibiting composition comprising at least one aromatic triazole, at least one molybdate salt and at least one nitrate salt.

The corrosion inhibiting composition may be present in an amount of 1.5 - 15% by weight based on the total weight of the biocidal composition, preferably including 0.5 - 5% by weight of each of the aromatic triazole, the molybdate salt and the nitrate salt.

The strong oxidising agent may be selected from the group consisting of monopersulphates, persulphates, perborates, hydrogen peroxide/ peracetic acid, benzoyl peroxide, permanganates, nitrates, and chlorous/hypochlorous acid. Preferred oxidising agents are monopersulfates. The oxidising agent may be included in an amount of 40 - 95% by weight, based on the total weight of the biocidal composition.

The biocidal composition may also include at least one water-soluble acid, the acid being selected for compatibility with the oxidising agent to maintain the appropriate pH.

In a composition containing monopersulphates such as potassium monopersulphate, the acid is preferably selected from the group consisting of malic acid, sulfamic acid, citric acid, lactic acid, sorbic acid, benzoic acid, salicylic acid, boric acid, glycolic acid and mixtures thereof. Most preferably, the acids are a mixture of malic acid, sulfamic acid and citric acid.

The biocidal composition may also include surfactants and free flow agents.

A preferred biocidal composition comprises:

- (a) 40- 95% potassium monopersulfate (commercial grade);
- (b) 1.5- 30% of at least one water-soluble acid selected from the group consisting of malic acid, sulfamic acid, citric acid, lactic acid, sorbic acid, benzoic acid, salicylic acid, boric acid and glycolic acid;
- (c) 0.5- 10% nonionic surfactant;

(d) 1.5-15% corrosion inhibiting composition comprising benzotriazole, sodium molybdate and sodium nitrate.

The water-soluble acid is preferably a mixture of malic acid, sulfamic acid and citric acid.

5 Citric acid in particular, when solubilised with monopotassium persulphate provides excellent chelating properties and increases the permeability of the outer membrane of bacteria, particularly gram-negative bacteria. The acid accelerates the formation of nascent oxygen and boosts the reactivity of the oxygen with the cell's metabolism. It promotes the  
10 increase in speed of the metabolism to the detriment of the cell.

The combination of citric acid and the oxidising agent at the % stated aids the direct reaction of the molecular structure of the cell's proteins and interferes with enzyme reactions.

The nonionic surfactant may be selected from disulfonated anion  
15 surfactants, such as, DOWFAX 20B102 or alkyl polyether alcohol surfactants, such as, Triton DF16.

The sensitivity of the made up solution to trace metals and organic matter is also reduced, thus improving the useable life of the solution.

The composition preferably also includes 0.1 - 5% of a free flow  
20 agent such as fumed silicon dioxide.

The biocidal composition is usually made up in powder form and is diluted in deionised water for use, preferably to a concentration of 2.5-7.5% w/v more preferably 5% w/v. The pH of the made up solution is approximately 2.0.

25 In a third aspect the present invention provides a method of reducing corrosivity of a strong oxidising agent characterised in that a strong oxidising agent is used in conjunction with a corrosion inhibiting composition comprising at least one aromatic triazole, at least one molybdate salt and at least one nitrate salt. Preferably the corrosion inhibiting composition  
30 comprises benzotriazole, an alkali metal molybdate salt such as sodium molybdate and an alkali metal nitrate salt such as sodium nitrate. The corrosion inhibiting composition may also include a free flow agent such as fumed silicon dioxide.

35 In a fourth aspect the present invention provides the use of the corrosion inhibiting composition of the first aspect of the invention for reducing the corrosivity of a strong oxidising agent.

In a fifth aspect the present invention provides a method of cleaning and sterilising a surface comprising contacting the surface with a strong oxidising agent and a corrosion inhibiting composition, said corrosion inhibiting composition comprising at least one aromatic triazole, at least one molybdate salt and at least one nitrate salt.

The surface may be selected from plastics, carbon steel and metals including brass, aluminium, copper and alloys thereof and stainless steel. The surface may comprise at least in part, one or more surfaces. The surfaces will be at least partially protected from corrosion which may otherwise occur in the presence of the oxidising agent. Preferably the surfaces are selected from metals.

#### **Brief Description of the Drawings**

Figure 1 is a graph of measured anodic current vs applied potential for a brass electrode for a 5% w/v solution of a composition of the present invention.

Figure 2 is a graph of measured anodic current vs applied potential for a brass electrode for a 5% w/v solution of a reference composition used for comparative purposes.

Figure 3 is a graph of measured anodic current vs applied potential for an aluminium electrode comparing a 5% w/v solution of a composition of the present invention with a reference composition.

Figures 4 and 5 are graphs similar to Fig. 3 using an aluminium alloy electrode.

Figures 6 and 7 are graphs similar to Fig. 3 using stainless steel electrodes.

In order that the invention be more clearly understood, preferred forms thereof will now be described with reference to the following examples.

#### **Best Modes**

The most straightforward electrochemical procedure has been applied in conjunction with the microscope examination of materials before and after testing. When driven electrochemically to corrosion during testing, the mode of degradation observed was by pitting. Consequently, estimates of "corrosion current" are not meaningful because the current densities depend on the specific areas of electrochemical activity which are not

readily measurable and, indeed are changing continually both in number and extent.

The test involves imposing on the test specimen a steadily increasing aggressive potential and observing the resulting anodic current. (This is a potentiodynamic procedure.) Until active corrosion (pitting) occurs, low anodic currents allow some comparison of the respective stabilities of metallic components and the likelihood of galvanic effects. The potential corresponding to the establishment of pitting is a measure of the effectiveness of the intrinsic passivity or of inhibition. In practice, a single open cell is used which contains the test piece, suitably mounted as an electrode, a calomel reference electrode and an iridium counter electrode. The potential between the test electrode and the reference is monitored and controlled by a Solartron Instruments Electrochemical Interface (Type 1286) which supplies the measured and recorded corrosion current via the Iridium electrode. This instrument is computer controlled, either by a Hewlett Packard 9000/216 with Solartron software 1090 or an IBM PS2 system 80 with University written software for data logging, electrochemical control and graphic outputs.

Test electrodes are immersed in the electrolyte until the open circuit potential stabilises. The potential is then swept anodically until passivation or inhibition breaks down. It is an important feature of the experiment that the applied potential should change slowly (typically  $0.5 \text{ mV Sec}^{-1}$ ) to allow the surface phases to respond.

In the present tests, the cell is held at  $20^{\circ}\text{C}$ . The metals to be tested were immersed in the electrolyte solutions described below for 2 hour periods.

The electrolytes correspond to biocidal compositions. A corrosion inhibiting composition according to the present invention (shown below as (A)) and a comparative reference composition (B), containing a corrosion inhibiting composition outside the scope of the present invention, were added to the biocidal composition.

<b>Biocidal composition:</b>	<b>Qty w/w</b>
Potassium monopersulfate (commercial grade)	82.5%
Citric acid (ANH)	9.0%
Malic acid	0.5%
Sulfamic acid (ANH)	0.5%
Nonionic surfactant	7.5%

The above biocidal composition is added to the following compositions, (A) and (B):

5

**(A) Corrosion Inhibiting composition of the invention:**

	Qty w/w based on total weight of biocidal composition
Sodium nitrate	1.0%
Sodium molybdate	0.5%
Benzotriazole	0.5%

**(B) Comparative Corrosion Inhibiting composition:**

10

	Qty w/w based on total weight of biocidal composition
Sodium nitrite	3%
Sodium molybdate	1.5%
Benzotriazole	1.0%

The resulting compositions are diluted with deionised water to a concentration of 5% w/w to form the electrolytes and the corrosiveness of each solution was compared using the potentiodynamic test described above.

15

The results of the test were assessed with reference to Figures 1 to 7.

For the comparative composition (B), the electrolyte is aggressive towards brass and copper but harmless to stainless steel. In practical use, for an item comprising stainless steel as well as brass, there would be a risk



of contamination of the stainless steel components with corrosion products from brass. This could lead to harmful galvanic effects.

For the composition of the present invention (A) there is a dramatic improvement in the performance of brass, aluminium and aluminium alloy.

- 5 Good corrosion inhibition is also found on the stainless steels. The combination of sodium nitrate with sodium molybdate and benzotriazole has a synergistic effect giving improved performance and allowing active levels to be reduced.

- 10 When used in conjunction with a strong oxidising agent, the reduction of corrosion inhibitor levels allows more oxidising agent to be present thus boosting biocidal activity.

- 15 It will be appreciated by persons skilled in the art that numerous variations and/or modifications may be made to the invention as shown in the specific embodiments without departing from the spirit or scope of the invention as broadly described. The present embodiments are, therefore, to be considered in all respects as illustrative and not restrictive.

## CLAIMS

1. A corrosion inhibiting composition for use in combination with a strong oxidising agent, said composition comprising at least one aromatic triazole, at least one molybdate salt and at least one nitrate salt.
- 5 2. A corrosion inhibiting composition according to claim 1 wherein the aromatic triazole is selected from benzotriazole and tolyltriazole.
3. A corrosion inhibiting composition according to claim 1 wherein the molybdate salts are alkali metal salts, preferably sodium molybdate.
4. A corrosion inhibiting composition according to claim 1 wherein the  
10 nitrate salts are selected from alkali metal salts, preferably sodium nitrate.
5. A corrosion inhibiting composition according to any of the preceding claims which additionally includes a free-flow agent.
6. A corrosion inhibiting composition according to claim 5 wherein the free-flow agent is silicon dioxide.
- 15 7. A corrosion inhibiting composition according to claim 6 wherein the silicon dioxide is fumed silicon dioxide.
8. A biocidal composition comprising a strong oxidising agent and a corrosion inhibiting composition according to any one of the preceding claims.
- 20 9. A biocidal composition according to claim 8 wherein the corrosion inhibiting composition is present in an amount of 1.5 to 15% by weight based on the total weight of the biocidal composition.
10. A biocidal composition according to claim 9 wherein the corrosion inhibiting composition includes 0.5 to 5% by weight of each of the aromatic  
25 triazole, the molybdate salt and the nitrate salt.
11. A biocidal composition according to any one of claims 8 to 10 wherein the strong oxidising agent is selected from the group consisting of monopersulphates, persulphates, perborates, hydrogen peroxide/peracetic acid, benzoyl peroxide, permanganates, nitrates, and chlorous/hypochlorous  
30 acids.
12. A biocidal composition according to any one of claims 9 to 11 wherein the oxidising agent is in an amount of 40 to 95% by weight, based on the total weight of the biocidal composition.
13. A biocidal composition according to any one of claims 9 to 12, which  
35 further comprises at least one water-soluble acid.

14. A biocidal composition according to claim 13 wherein the acid is selected from the group consisting of maleic acid, sulfamic acid, citric acid, lactic acid, sorbic acid, benzoic acid, salicylic acid, boric acid, glycolic acid.
15. A biocidal composition according to any one of claims 8 to 14 which  
5 further includes surfactants and free flow agents.
16. A biocidal composition comprising :
- (a) 40-95% potassium monopersulphate
- (b) 1.5-30% of at least one water-soluble acid selected from the group  
10 consisting of malic acid, sulfamic acid, citric acid, lactic acid, sorbic acid, benzoic acid, salicylic acid, boric acid and glycolic acid;
- (c) 0.5-10% nonionic surfactant;
- (d) 1.5-15% corrosion inhibiting composition comprising benzotriazole, sodium molybdate and sodium nitrate.
17. A biocidal composition according to claim 16 wherein the water  
15 soluble acid is a mixture of malic, sulfamic and citric acid.
18. A biocidal composition according to claim 16 or 17 which further comprises 0.1 to 5% w/w of free flow agent, preferably silicon dioxide.
19. A biocidal composition according to any one of claims 16 to 18 where the concentration is 2.5 to 7-5 %w/v and wherein the pH is  
20 approximately 2.0.
20. A method of reducing corrosivity of a strong oxidising agent characterised in that a strong oxidising agent is used in conjunction with a corrosion inhibiting composition according to any one of claims 1 to 7.
21. Use of the corrosion inhibiting composition according to any one of  
25 claims 1 to 7 for reducing the corrosivity of a strong oxidising agent.
22. A method of cleaning and sterilising a surface comprising contacting the surface with a strong oxidising agent and a corrosion inhibiting composition according to any one of claims 1 to 7.
23. A method according to claim 22 wherein the surface may comprise  
30 at least in part, one or more metal surfaces.

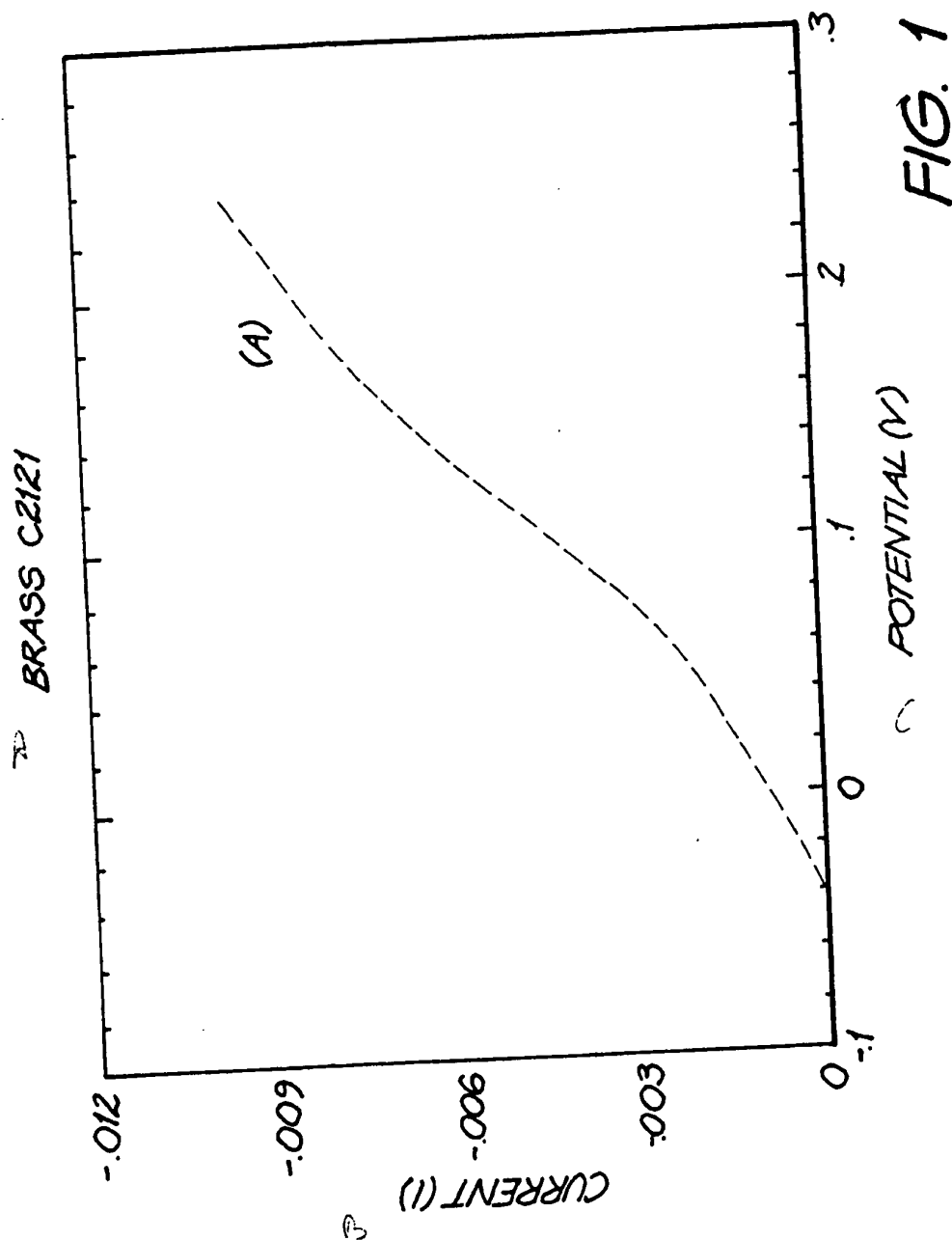


FIG. 1

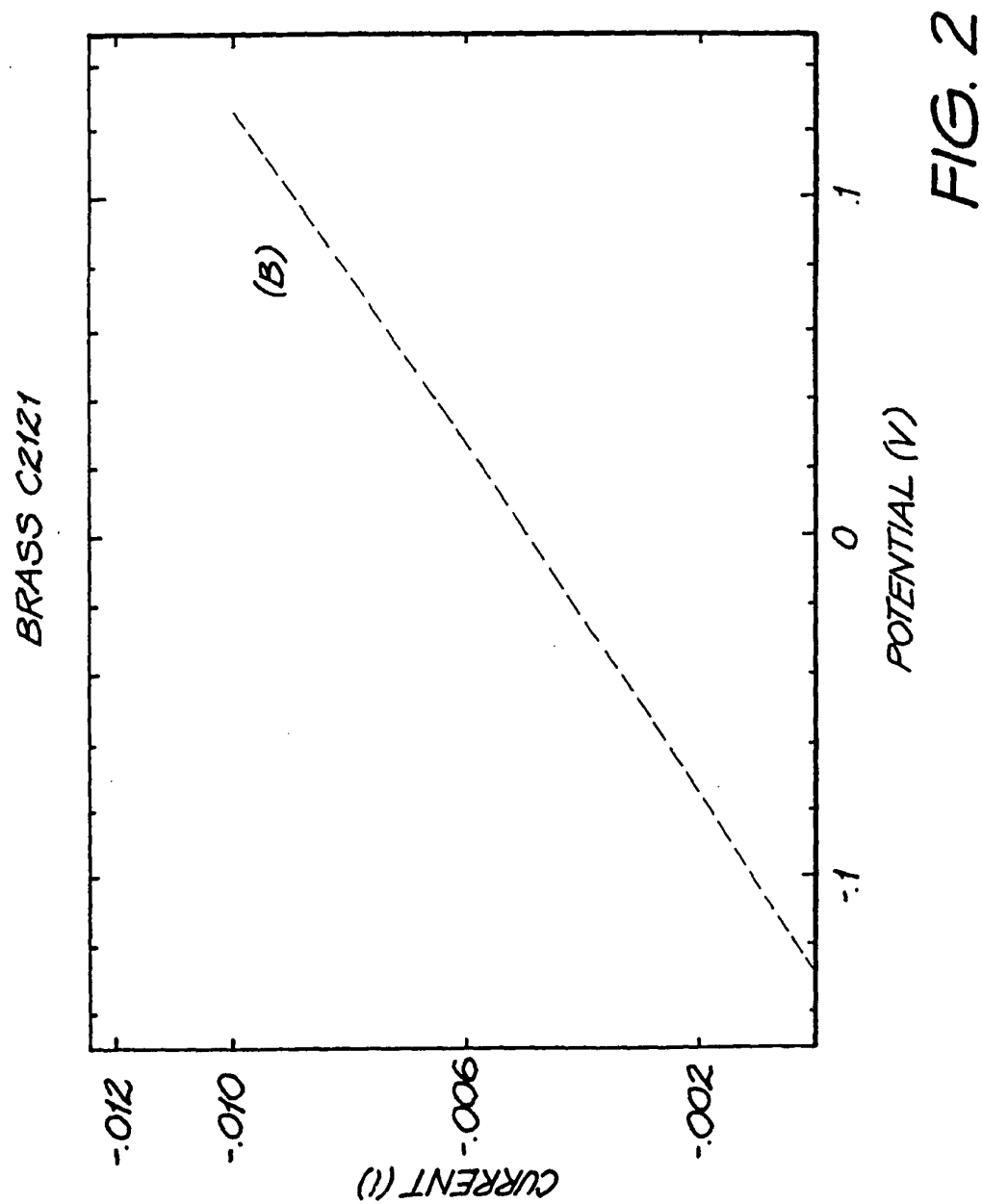


FIG. 2

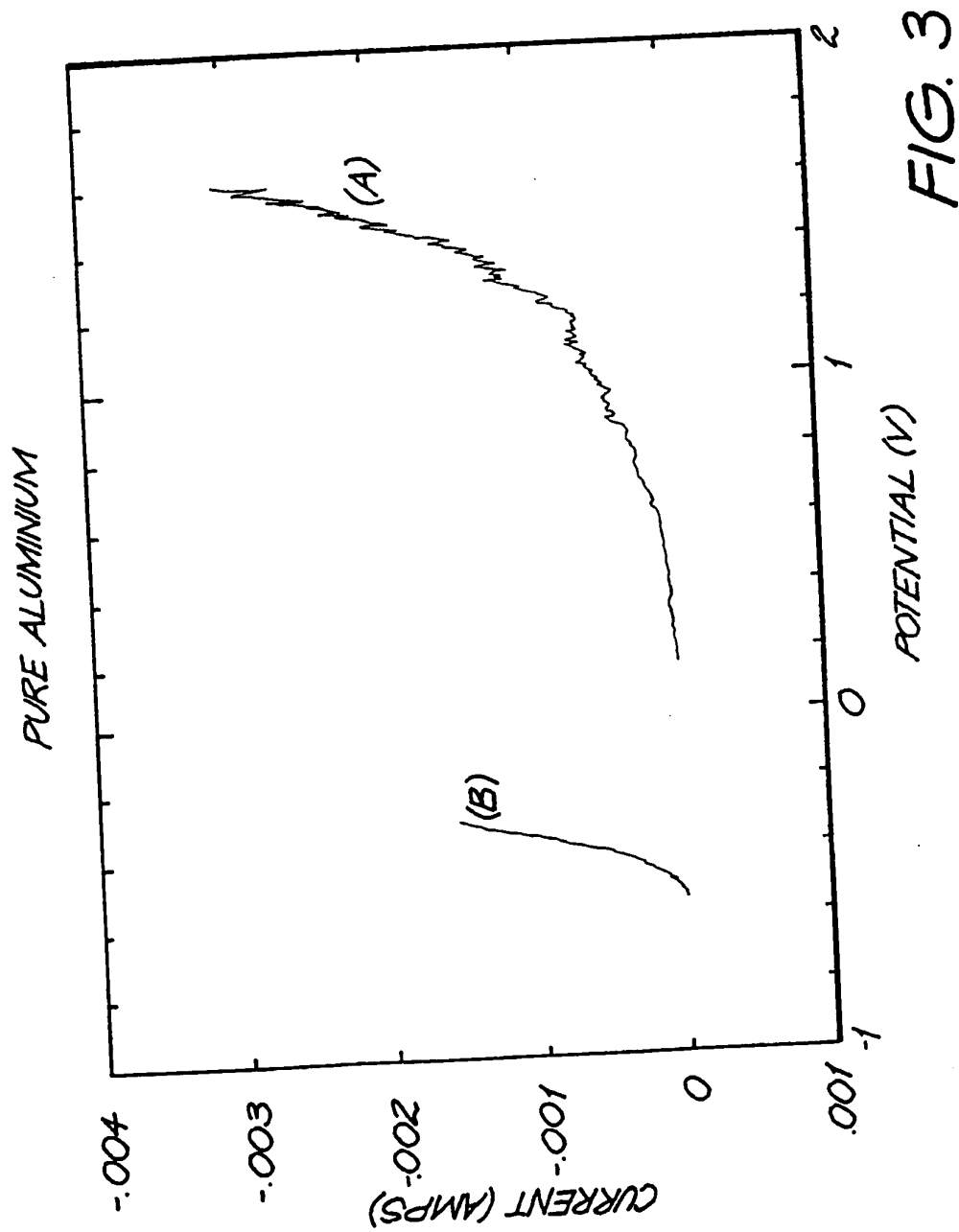


FIG. 3

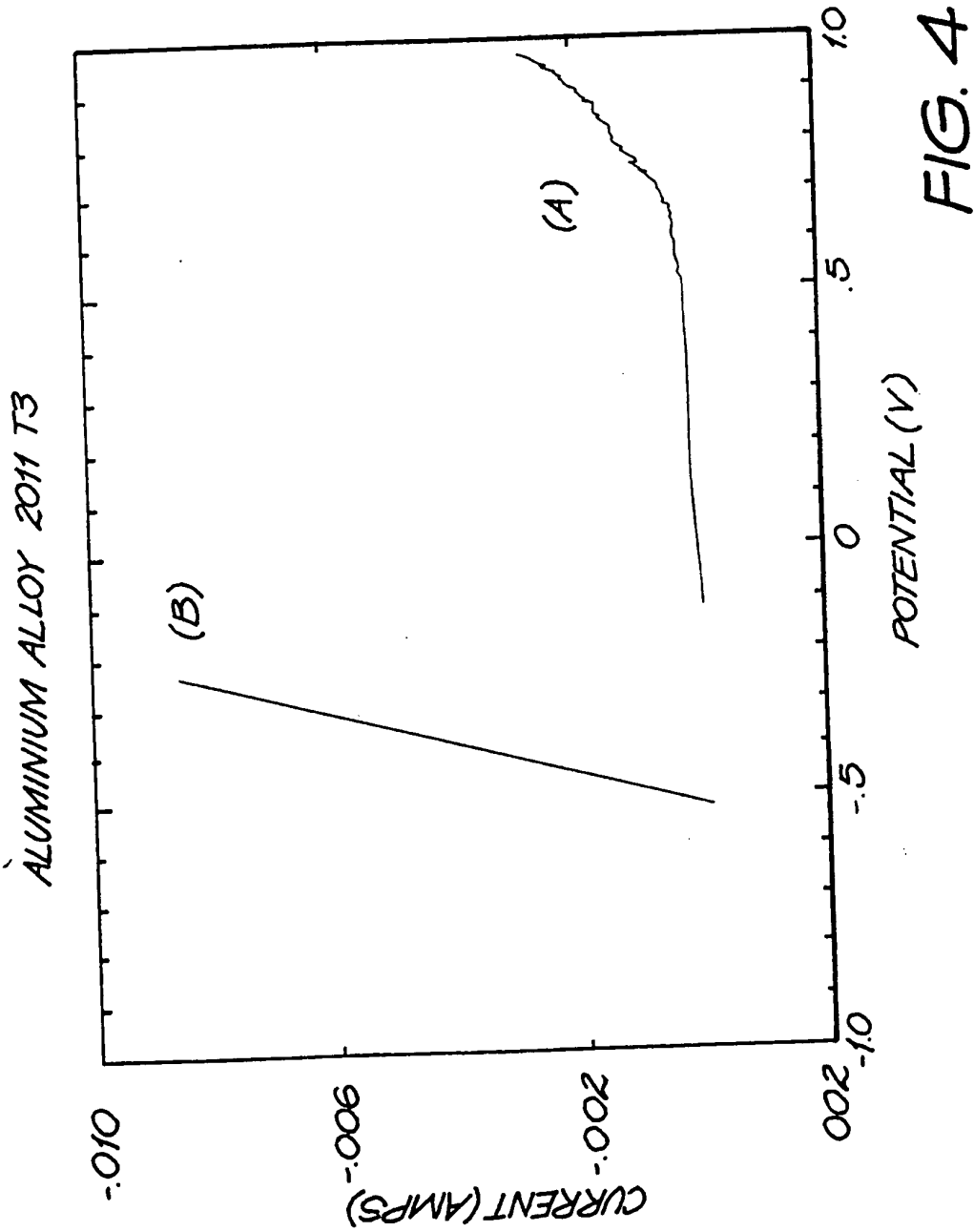


FIG. 4

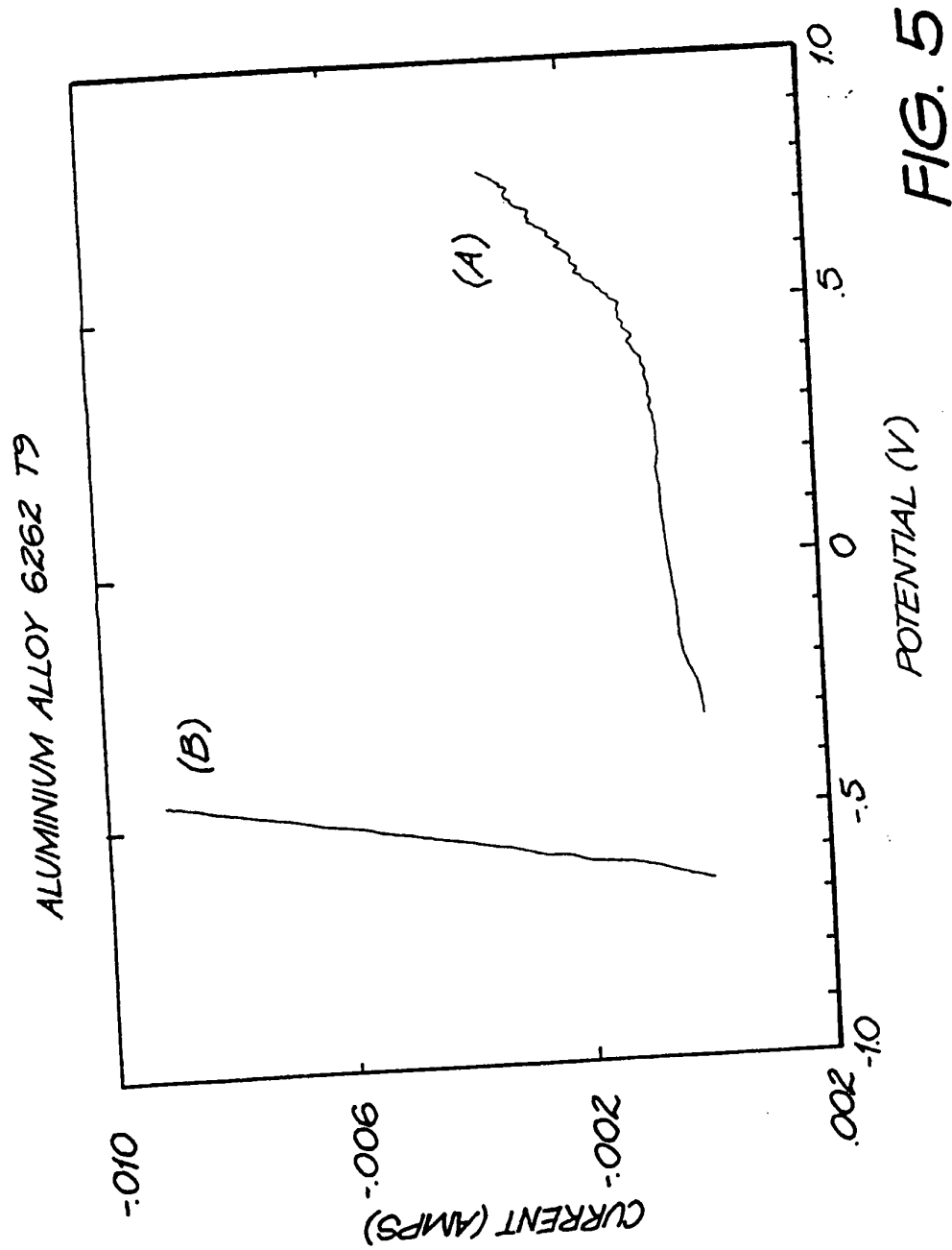
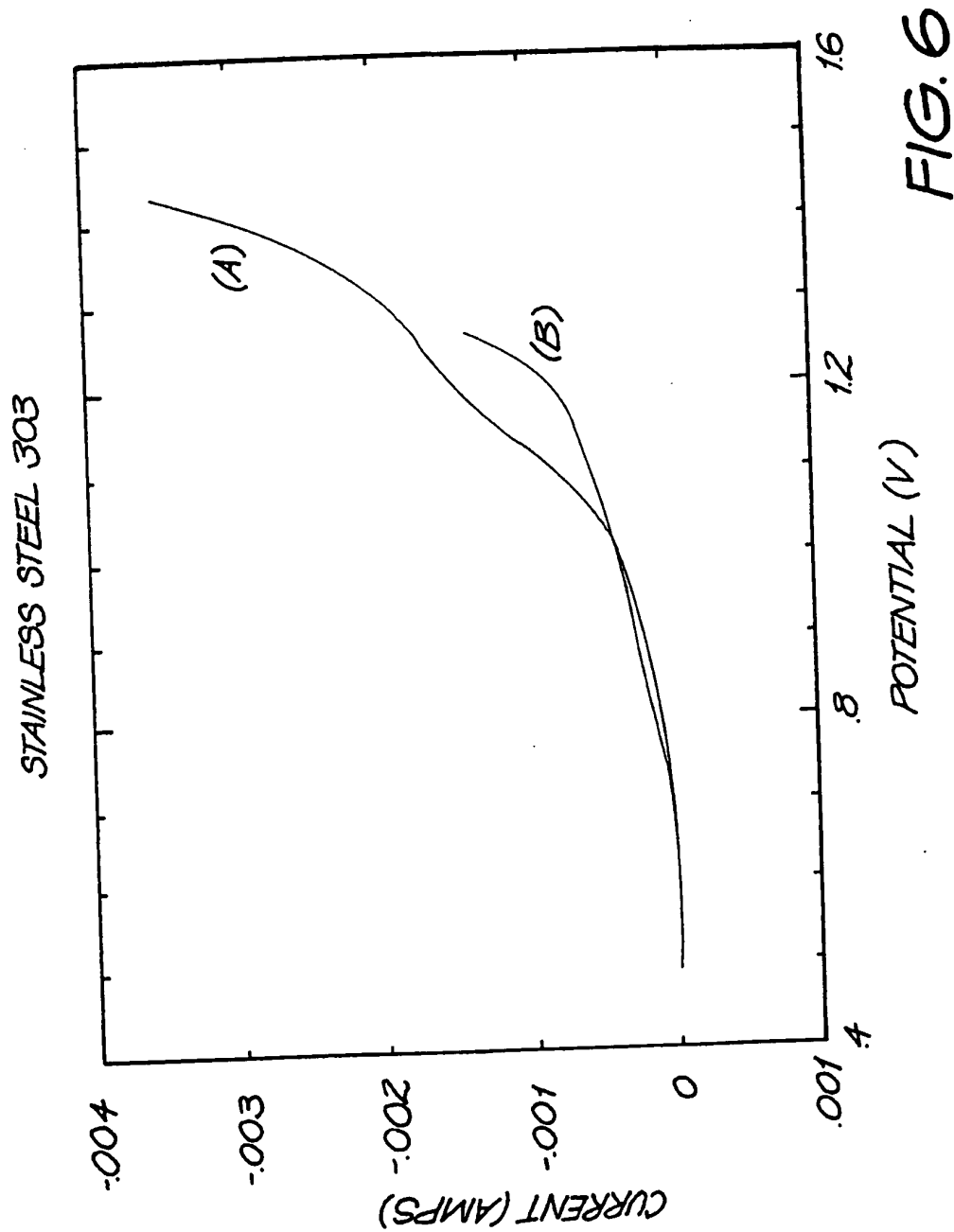


FIG. 5





STAINLESS STEEL 316

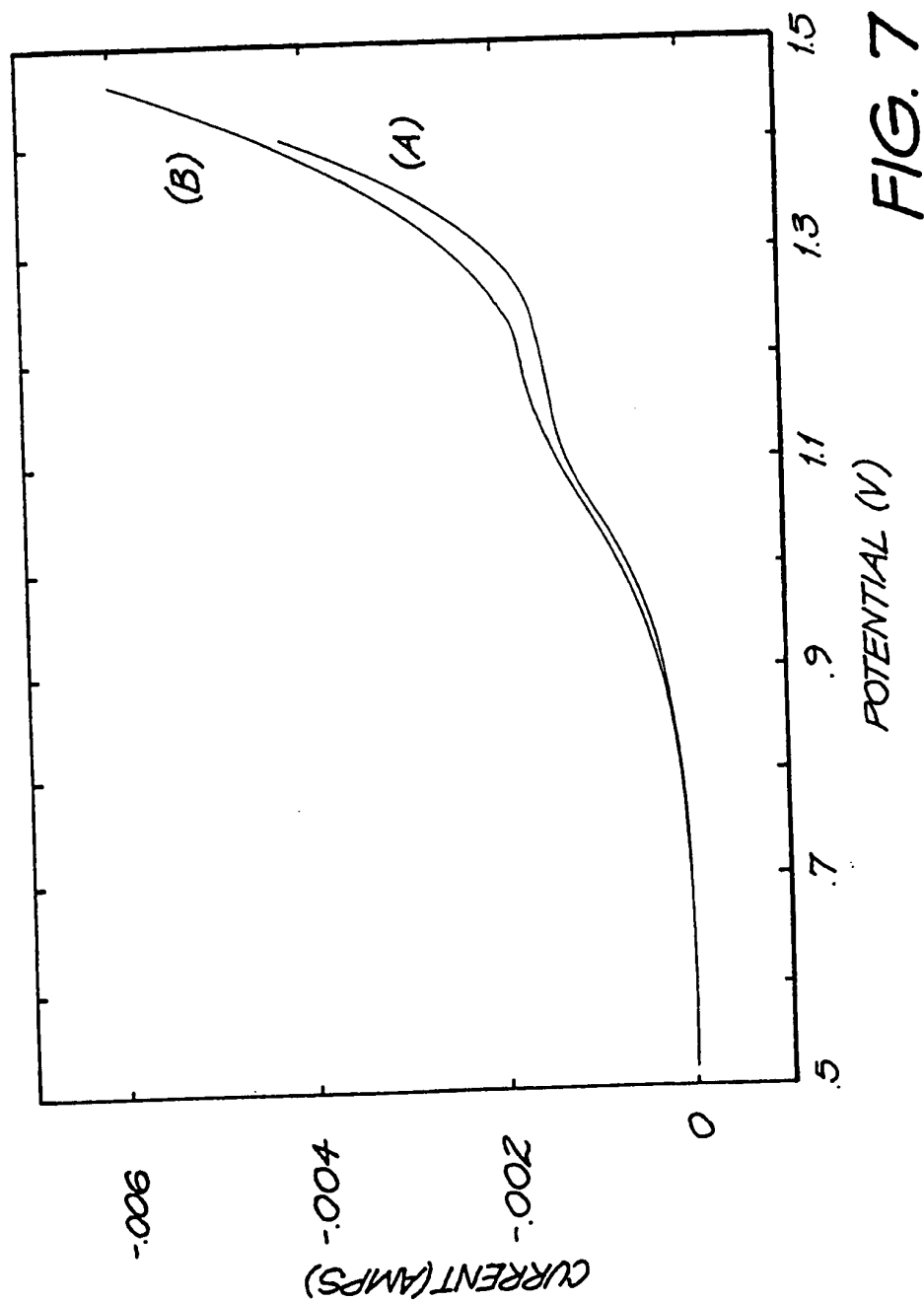



FIG. 7

## INTERNATIONAL SEARCH REPORT

International Application No.

PCT/AU 97/00784

<b>A. CLASSIFICATION OF SUBJECT MATTER</b>		
Int Cl <sup>6</sup> : C09K 15/30, 15/02; C23F 11/14, 11/18, 11/173		
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<b>B. FIELDS SEARCHED</b>		
Minimum documentation searched (classification system followed by classification symbols)		
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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
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<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4728452 A (HANSEN) 1 March 1998	1-4
Y	Whole document	1-4, 8-14, 16, 17, 19-23
X	WO 95/07323 A (EVANS COOLING SYSTEMS INC) 16 March 1995	1-4
Y	Whole document	1-4, 8-14, 16, 17, 19-23
X	JP 07157887 A (SEIKEN KAGAKU KOGYO KK) 20 June 1995	1-4
Y	Abstract	1-4, 8-14, 16, 17, 19-23
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C <input checked="" type="checkbox"/> See patent family annex		
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Date of the actual completion of the international search 13 January 1998		Date of mailing of the international search report 23 JAN 1998
Name and mailing address of the ISA/AU AUSTRALIAN INDUSTRIAL PROPERTY ORGANISATION PO BOX 200 WODEN ACT 2606 AUSTRALIA Facsimile No.: (02) 6285 3929		Authorized officer  DAVID K. BELL Telephone No.: (02) 6283 2309

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International Application No.  
PCT/AU 97/00784

C (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
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Y	EP 357238 A2 (STERIS CORPORATION) 7 March 1990 Whole document	1-4, 8-14, 16, 17, 19-23
Y	US 5545343 A (BROUGHAM et al) 13 August 1996 Whole document	1-4, 8-14, 16, 17, 19-23
Y	GB 2292687 A (GREEN) 6 March 1996 Whole document	1-4, 8-14, 16, 17, 19-23

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GB	2292687	NONE					

END OF ANNEX

# INTERNATIONAL SEARCH REPORT

## Information on patent family members

International Application No.  
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This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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		WO	95/20406		
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